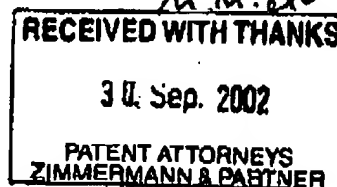


GR 97 P 2734

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT : Frank Hintermaier
Applic. No. : 09/161,196
Filed : September 25, 1998
Title : Capacitor Having A Barrier Layer Made Of A
Transistion Metal Phosphide, Arsenide Or
Sulfide
Examiner : Cuong Q. Nguyen
Group Art Unit : 2811

DECLARATION under 37 C.F.R. § 1.132

The undersigned Dr. Rainer Bruchhaus hereby declares:

He studied chemistry and mineralogy in Munich, Germany and received his diploma in chemistry and mineralogy in 1980 and 1984, respectively. After receiving his diploma in chemistry, he studied as a postgraduate student in Munich, Germany from 1980 to 1983 and received a Doctorate in chemistry in 1983.

After leaving university he joined the Siemens AG in August 1984 and began working on the development of ceramic varistors in the ceramics department of Corporate Technology in Munich. From 1987 to 1989 he worked in the field of high temperature superconductors in the ceramics department of Siemens Corporate Technology. Since 1989 he has been working in the field of ferroelectric thin films. From 1989 to 1993 this work focused on the deposition of PZT thin films as well as suitable metal electrodes, the patterning of these films using photolithography and the

electrical characterization of these films in terms of hysteresis loops, leakage current, and ferroelectric switching behavior. Since 1993 managed a 3 years project together with partners from industry as well as university. This project is funded by the German Government for the application of ferroelectric lead zirconate titanate (PZT) thin films in bulk micromachined pyroelectric detector arrays. From 1997 to 2000 he was responsible for a funded project on the application of pyroelectric thin films in infrared detector arrays using CMOS compatible surface micromechanics in cooperation with Oaram Optoelectronics and Infineon Technologies, AG as industrial partners. In addition, he worked together with Infineon Technologies AG on the development of barrier layers and bottom electrode materials for capacitor on plug structures. In 2001 he joined Infineon Technologies and is currently delegated to Infineon Technologies Japan K.K. where he is working in the development of high density ferroelectric memory devices in a joint project with Toshiba Corporation in Japan. He is a principal engineer in the integration department responsible for the ferroelectric capacitor module. This long term experience in the field of ferroelectric thin films including electrode as well as barrier materials resulted in invitations to presentations on international conferences. He authored and co-authored more than 20 papers in the field of ferroelectric thin films,

which establishes him as an expert in the relevant field.

The undersigned declares that he has studied the art disclosed in the US-Patent 5,691,219 to Kawakubo et al., and based on the technical expertise of the undersigned declares that the US-Patent 5,691,219 does not disclose a capacitor comprising a barrier layer disposed below a

capacitor dielectric, said barrier layer consisting essentially of a compound formed from a transition element and a material selected from the group consisting of phosphorus, sulfur, and arsenic.

US 5,691,219 describes, with reference to Figures 4A to 4E on column 7, line 35 to 60 of the specification, a memory cell comprising a contact plug 11 formed in an insulating layer 9. The contact plug consists of polysilicon that was deposited by a LPCVD method into a contact hole previously formed in the insulating layer 9. Phosphorous was diffused into the polysilicon deposited in the contact hole thereby decreasing the resistivity of the polysilicon to 10 to 100 Ω/\square . After forming a trench in the layers 9 and 10, as shown in Figure 4C, the barrier metal film 12 made of titanium nitride was formed partly on the polishing stop layer 10 and partly on the inner surface of the trench. It is pointed out in US 5,691,219 that the barrier metal layer can also be made of titanium, tantalum or tantalum nitride or the like.

Based on his scientific and work experience, the undersigned is convinced that the concentration of phosphorus atoms used as a dopant for a plug is far too low to create a TiP barrier layer in case only titanium and no additional phosphorus atoms are present. This also applies to the case that the barrier metal layer is made of tantalum. Again, the concentration of phosphorus atoms used as a dopant for a plug is far too low to create a TaP barrier layer in case only tantalum and no additional phosphorus atoms are present.

The undersigned declares that all statements made herein of his own knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable

by fine or imprisonment, or both, under 18 U.S.C § 1001 and such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Rainer Buchhaus

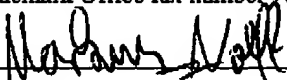
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CERTIFICATION OF FACSIMILE TRANSMISSION

I hereby certify that this paper for Serial No. 09/161,196 is being facsimile transmitted to the Patent and Trademark Office fax number 703 308 7722 on the date shown below.



Signature

October 4, 2002
Date

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Before the Board of Patent Appeals and Interferences

Inventor : Frank Hintermaier
Applic. No. : 09/161,196
Filed : September 25, 1998
Title : Capacitor Having a Barrier Layer Made of a Transition Metal
Phosphide, Arsenide Or Sulfide
Examiner : Cuong Q. Nguyen Art Unit: 2811

CONDITIONAL NOTICE OF APPEAL FROM THE PRIMARY EXAMINER TO THE
BOARD OF PATENT APPEALS AND INTERFERENCES

Hon. Commissioner of Patents and Trademarks,
Washington, D. C. 20231

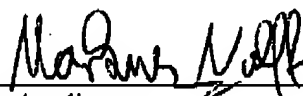
Sir:

Applicant hereby appeals to the Board of Patent Appeals and Interferences from the decision dated June 4, 2002 of the Primary Examiner finally rejecting claims 1, 3, 5 and 7-12.

This Notice of Appeal is to be entered only if all of the rejected claims are not allowed as a result of the amendment being simultaneously filed herewith.

The Patent and Trademark Office is hereby given authority to charge Deposit Account No. 12-1099 of Lerner and Greenberg, P.A. for the \$310.00 appeal fee (if required) and any fees due or deficiencies of payments made for any purpose during the pendency of the above-identified application.

Respectfully submitted,



For Applicant

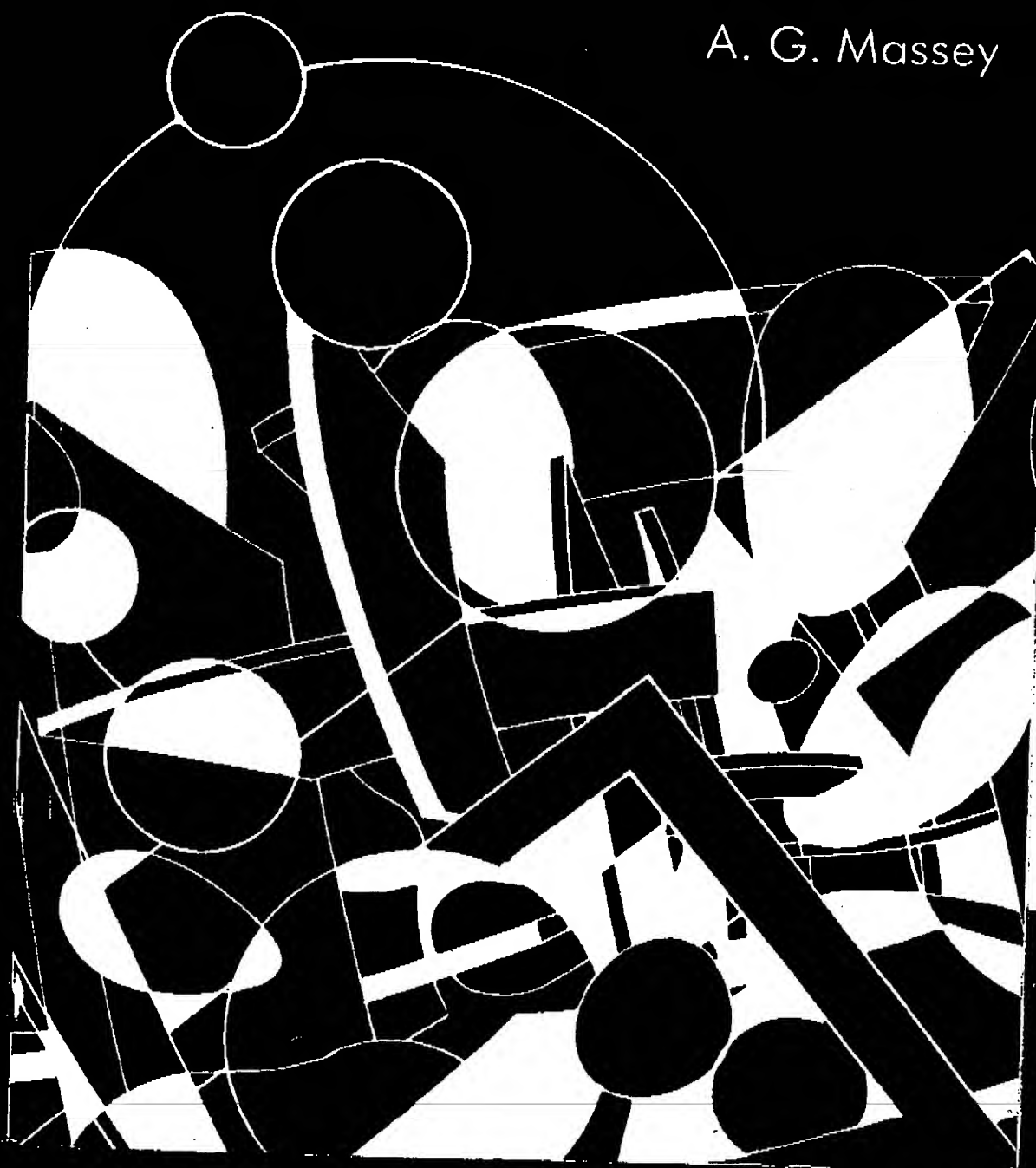
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Chapter 1

The Periodic Table

SCHRÖDINGER'S WAVE EQUATION AND QUANTUM NUMBERS

Classical laws which adequately describe movement of macroscopic bodies break down at the atomic level as a consequence of Heisenberg's uncertainty principle: it is fundamentally impossible to know precisely the values of *both* the energy and position of an electron in an atom. Hence, since the electron's energy can be measured very accurately using spectroscopy, we can only have a statistical, or probability, knowledge of its position. For submicroscopic species the wave characteristics described by de Broglie become important and a mathematical science developed by Schrödinger, called wave mechanics, must be used to describe their motion.

Although solutions can be found to wave mechanical equations describing one-electron systems such as H, He⁺ and Li²⁺, it has proved impossible to solve such equations for multi-electron atoms. The reader should realize that the orbitals described later in this chapter and used throughout chemistry are those calculated for the hydrogen atom: they are *assumed* to remain unchanged for all other elements in the periodic table.

When writing the wave equation for the hydrogen atom, Schrödinger considered the electron as a three-dimensional standing wave and connected the wavefunction ψ to the total electronic energy E by the expression

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 \mu}{h^2} \left(E + \frac{e^2}{r} \right) \psi = 0$$

where μ is the reduced mass of the electron and its polar coordinates are as shown in Fig. 1. Fortunately chemists do not need to understand this equation in order to use the results of its solution for E and ψ . The wavefunction, or *orbital*, ψ has no physical significance and hence we are unable to make a meaningful model of it. However, since ψ is an amplitude function, Schrödinger, and Born, suggested that ψ^2 measures the intensity of the electron wave, and from this idea it has become common practice to describe an orbital in terms of a smeared-out 'electron cloud'

The periodic table

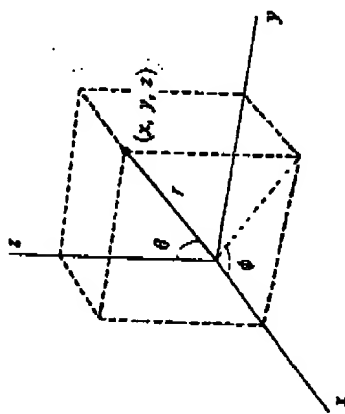


Fig. 1—The position of the electron in the hydrogen atom relative to the nucleus, in terms of Cartesian and polar coordinates. The nucleus is at the origin (0, 0, 0). $z = r \cos \theta$, $y = r \sin \theta \sin \phi$, $x = r \sin \theta \cos \phi$.

having a probability, or density, equal to ψ^2 at any given point. It is found that the allowed values of the electronic energy E are governed by four quantum numbers. The principal quantum number n summarizes the predominant part of an orbital's energy whilst the secondary (or azimuthal) quantum number l and the magnetic quantum number m_l mainly describe the shape and orientation of a particular electron orbital in space; a fourth quantum number m_s describes the 'spin' state of the electron. These quantum numbers may take a range of values, but once n has been chosen the corresponding values of l and m_l are defined by the following relationships:

n can be any whole number from one to infinity: 1, 2, 3, ..., ∞ .

l is then limited to 0, 1, 2, 3, ..., $n-1$.

m_l , being governed by l as its subscript suggests, has the values 0, ± 1 , ± 2 , ..., $\pm l$. m_s is limited to $+\frac{1}{2}$ and $-\frac{1}{2}$.

The quantum numbers* are widely used in shorthand notation to label orbitals: orbitals having $l=0$ are called s orbitals whilst those with $l=1$, 2 or 3 are p, d or f orbitals respectively. After $l=3$ the letters follow in alphabetical sequence so that orbitals having $l=4$ are g orbitals, those having $l=5$ are h orbitals, etc. However, only s, p, d and f orbitals are of chemical significance and we may ignore the others. A numerical prefix to the orbital letter describes the principal quantum number to which the orbital belongs: a 2s orbital is one having $n=2$ and $l=0$, and a 3d orbital has $n=3$, $l=2$ for example. Although basically the periodic table is an array of the elements in order of their atomic number, it will be seen shortly that it is the Pauli exclusion principle which gives us an understanding as to why elements with similar chemical properties fall into such well-defined groups. One way of stating this principle is that no two electrons within the same atom may have an identical set of the four quantum numbers.

The sequence of orbital energies for the hydrogen atom is shown in Fig. 2. It will be noticed that the energies of the orbitals are negative. This implies that the energy

*The quantum numbers are, strictly, only legitimate for the single electron of a hydrogen atom. For polyelectron atoms the 'rest of the periodic table they are better regarded as simply being convenient labels for the various' ions.

Schrödinger's wave equation and quantum numbers

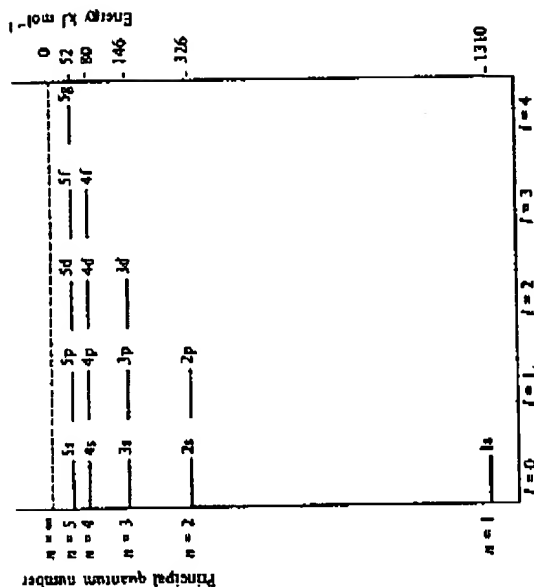


Fig. 2—Some electronic energy levels in the hydrogen atom. (Note: the energy of the n th level is equal to $-1310/n^2$ kJ mol $^{-1}$). As n increases the orbitals become larger and the electrons are further from the nucleus; by Coulomb's law this results in a lowering of the electron binding energy.

of the hydrogen atom, whether the atom is in the ground state ($n=1$) or an excited state ($n \geq 2$), is lower than the energy of the isolated electron and the isolated nucleus ($E=0$ kJ), a condition which is required for a stable atom.

The magnetic quantum number m_l may take values from $+l$ to $-l$, including zero. For an s orbital ($l=0$) m_l can only be zero, but for a p orbital ($l=1$) m_l has the values $+1$, 0, -1 , which means that there are always three p orbitals for $n \geq 2$. In the absence of a magnetic field the three p orbitals are degenerate (i.e. they have identical energies), but when a magnetic field is applied to the hydrogen atom this degeneracy is removed. This occurs because the orientation in space of the three p orbitals is different and therefore each orbital interacts with an applied magnetic field in a different manner (Fig. 3). Similarly, d orbitals and f orbitals are fivefold ($m_l=2, 1, 0, -1, -2$) and sevenfold ($m_l=3, 2, 1, 0, -1, -2, -3$) degenerate respectively.

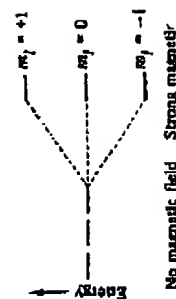


Fig. 3—The lifting of the degeneracy of p orbitals in a strong magnetic field.

The periodic table

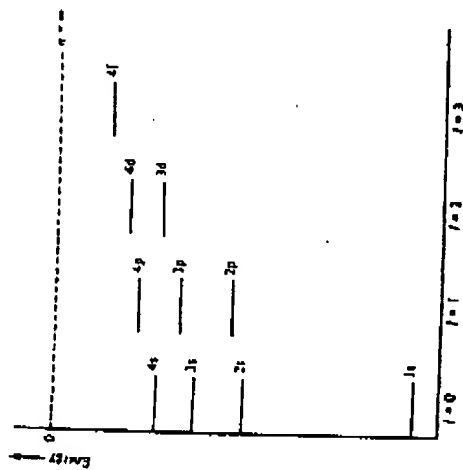


Fig. 4—The sequence of orbital energy levels for the lighter elements other than hydrogen.

From Fig. 2 it is obvious that, for the hydrogen atom, the s, p, d and f orbitals of a particular quantum shell are of equal energy—in other words, the energy of the orbitals is defined completely by the principal quantum number n . In all other atoms the energy of each orbital depends on both n and l ; the effect of this on the sequence of orbital energies for the light elements is shown in Fig. 4. To understand this partial dependence of the energy on the secondary quantum number l requires a discussion of orbitals.

s ORBITALS

All hydrogen s orbitals are spherically symmetrical because their wavefunctions contain no expression involving the angular coordinates θ and ϕ of the electron, as shown in the exponential equations for 1s and 2s orbitals:

$$\psi_{1s} = \left(\frac{1}{\pi a^3} \right)^{1/2} \exp \left(-\frac{r}{a} \right)$$

$$\psi_{2s} = \frac{1}{4} \left(\frac{1}{\pi a^3} \right)^{1/2} \left(2 - \frac{r}{a} \right) \exp \left(-\frac{r}{2a} \right)$$

where the constant a is known as the Bohr radius and is equal to 0.53 Å. Various ways of representing these wavefunctions are demonstrated in Fig. 5 and show clearly that we have only a statistical knowledge of the electron's whereabouts, as demanded by Heisenberg's uncertainty principle (because the energy of each orbital can be measured very precisely).

Of particular interest to chemists when studying the periodic table is the radial electron density $4\pi r^2 \psi^2$, which measures the electron density within the

s Orbitals

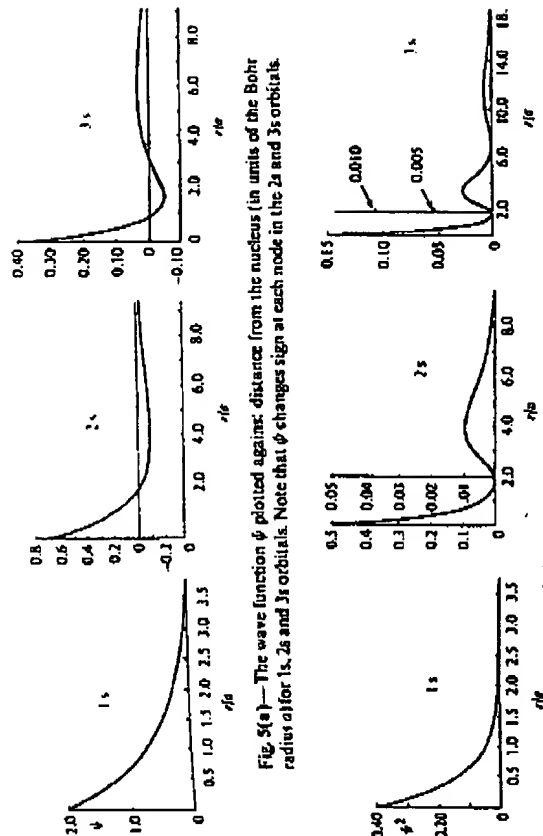


Fig. 5(a)—The wave function ψ plotted against distance from the nucleus (in units of the Bohr radius a) for 1s, 2s and 3s orbitals. Note that ψ changes sign at each node in the 2s and 3s orbitals.

Fig. 5(b)—The variation of ψ^2 with distance from the nucleus for 1s, 2s and 3s orbitals. Note the change in units on the ψ^2 axis for the outermost parts of the 2s and 3s orbitals. Since ψ^2 represents the probability of finding an electron at a particular point in an orbital, there is obviously a high electron density at, and close to, the nucleus for s orbitals; this contrasts sharply with all other orbital types (including p, d and f orbitals) in which ψ^2 is zero at the nucleus; see Fig. 8. [Figs 5(a) and 5(b) reproduced with permission from *Atoms and Molecules* by M. Karplus and R. N. Porter. Copyright 1970 Benjamin/Cummings Publishing Co.]

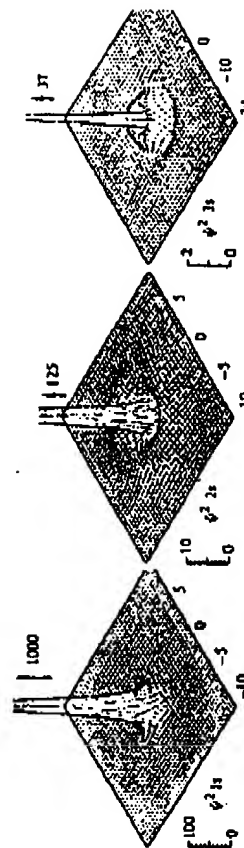


Fig. 5(c)—Computer simulations of the graphs shown in (b) rotated through 360° about the ψ^2 axis. [Reproduced with permission from *Journal of Chemical Education* vol. 47 (1970) p. 672.]

volume element $4\pi r^2 dr$ between two spheres, one of radius r and the other of infinitesimally larger radius $r + dr$. Unlike ψ^2 , which is the electron density per unit volume, this function is the probability of finding the electron at distance r from the nucleus summed over all directions (i.e. the electron density on the surface of a sphere of radius r). Plots of this radial function are given for the three orbitals in Fig. 6. The graphs are unusual in that there are two variables in the function on the y axis; for example, in the radial function for the 1s orbital, one variable is decreasing

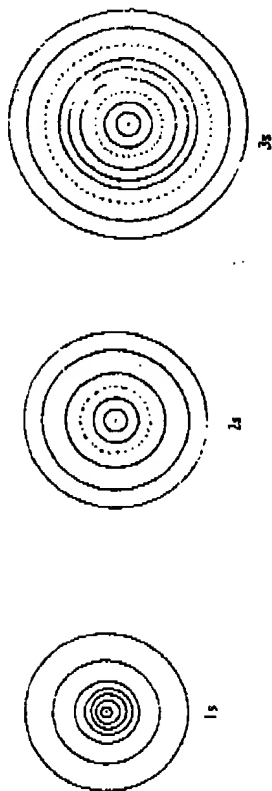


Fig. 5(d) — Contour diagrams of the electron density 'mountains and valleys' shown in (c) demonstrate the circular (or, in three dimensions, spherical) nature of s orbitals. More usually only the outer contour is drawn as a circle (sphere) encompassing some percentage (say 95%) of the total electron density; it is obvious from (b), (c) and (d) that the electron density within a spherical s orbital is not homogeneous.

exponentially whilst the other increases quadratically. At $r=0$, although ψ^2 is at a maximum, r^2 is zero and hence the radial function is also zero; at first the increase in r compensates for the decreasing electron density and the value of the radial distribution function rises. As r increases further the curve first reaches a maximum and then, as the (exponentially) decreasing ψ^2 becomes more and more dominant, it approaches zero asymptotically. Somewhat surprisingly the maximum occurs when r is 0.53 Å, which is identical to the radius calculated by Bohr for the first orbit of his planetary model of the hydrogen atom.

It should be noted from Fig. 6 that although the electron 'spends some of its time' further out from the nucleus the higher the value of n , there is still a finite chance of even a 3s electron being near to the nucleus as evidenced by the small 'humps' in the radial distribution curve. The electrons are said to *penetrate* close to the nucleus. The shapes of the ψ^2/r and $4\pi r^2 \psi^2/r$ graphs are particularly important because they show that the electron density distribution within the spherical s orbitals is not homogeneous.

Wavefunctions of the spherical s orbitals having $n > 1$ are zero at certain values of r (for example, owing to the $2 - r/a$ term in the 2s wavefunction given on page 40).

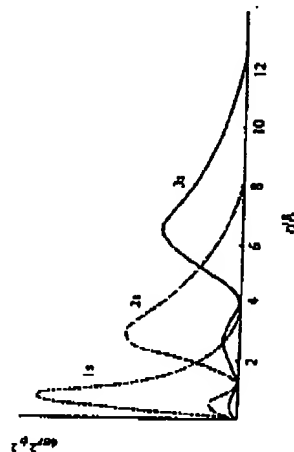


Fig. 6 — Rad. atom density functions for the 1s, 2s and 3s orbitals of a hydrogen atom.

This results in spherical nodal surfaces in these orbitals; at a node, besides the electron density being zero, the wavefunction ψ changes sign (Fig. 5). Although difficult to interpret in simple physical terms, the sign of ψ can be considered to describe the symmetry characteristics of the electron wave. Care should be taken to include symmetry signs on orbital diagrams because these properties of ψ are of primary importance when discussing bonding: only orbitals having wavefunctions with the same symmetry sign may 'overlap' to form a bond. In a rough analogy with light waves, two electron waves with the same ('vibrational') symmetry reinforce each other in the regions where they overlap, thus producing an increase in electron density in the region between the nuclei of the bonded atoms. When their symmetries are different the electron waves 'interfere', resulting in the formation of a node between the nuclei: Coulombic repulsion would then force the two nuclei apart because their positive charges are not shielded from each other by the electron cloud. Clearly this is an antibonding situation.

p and d ORBITALS

Unlike those of s orbitals, the wavefunctions for p and d orbitals depend on both r (the distance of the electron from the nucleus) and the angular coordinates of the electron, θ and ϕ , defined in Fig. 1. For example:

$$\psi_{2p_z} = \frac{1}{4} \left(\frac{1}{2\pi a^3} \right)^{1/2} \left[\frac{r}{a} \exp \left(-\frac{r}{2a} \right) \right] (\cos \theta)$$

$$\psi_{3d_{xy}} = \frac{1}{81} \left(\frac{1}{2\pi a^3} \right)^{1/2} \left[\left(\frac{r}{a} \right)^2 \exp \left(-\frac{r}{3a} \right) \right] (\sin^2 \theta \sin 2\phi)$$

i.e.

wavefunction = (a constant) \times (a radial part) \times (an angular part)

As can be seen, it is possible to divide these wavefunctions into two parts, one being the radial function $R(r)$ which contains an expression described only in terms of r and the other an angular function $A(\theta, \phi)$ which depends only on the direction defined by the angles θ and ϕ .

These two functions are normally interpreted in such a way that $R^2(r)$ describes the probability of finding the electron at a distance r from the nucleus but *without* defining direction, and $A^2(\theta, \phi)$ describes the probability of finding the electron in the direction θ, ϕ from the nucleus *regardless of the distance*.

A plot of $4\pi r^2 R^2(r)$ against r gives the variation of electron density with distance from the nucleus. From Fig. 7 it can be seen that, for a given principal quantum number, an s orbital spends more of its time close to the nucleus than does a p electron, and a p electron similarly spends more time near to the nucleus than does a d electron. Thus the penetration effect for electrons in the same quantum shell is in the order $s > p > d > f$.

It is the graphical plots of $A(\theta, \phi)$ or $A^2(\theta, \phi)$ which are usually shown when drawing diagrams of p and d orbitals. However, it should be realized that neither plot can represent the whole orbital because the radial part of the wavefunction is

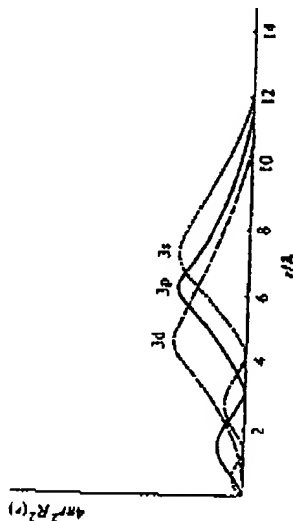


Fig. 7.—Radial electron density function for 3s, 3p and 3d orbitals of the hydrogen atom. Note that there are $n-1$ nodes in an s orbital, $n-2$ nodes in a p orbital and $n-3$ nodes in a d orbital for a given principal quantum number n .

ignored; therefore, stating that the 'orbitals' as drawn in Fig. 8 contain 90%, 95% or 99% of the electron density is meaningless because size cannot be represented without the inclusion of the radial function (as is done in the contour diagrams of ψ^2 shown in Fig. 8). Since the orbital nodes arise only in the radial part of the wave functions, the $A(\theta, \phi)$ plots for all p and d orbitals are the same as those shown in Fig. 8 for 2p and 3d, irrespective of the principal quantum number.

The radial distribution functions calculated for the various orbitals of the hydrogen atom necessarily correspond to the situation in which all the orbitals except the one under study are empty. In a multi-electron atom such as sodium, many of the orbitals

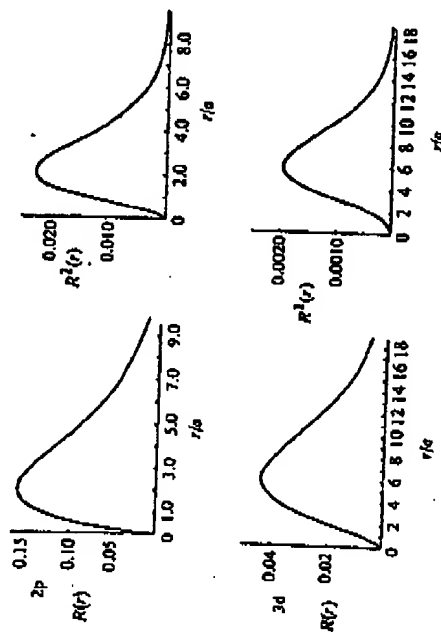


Fig. 8(a).—The variation of $R(r)$ and $R^2(r)$ with distance from the nucleus (in units of the Bohr radius) plotted for 2p and 3d orbitals. Both functions are zero at the nucleus because of the r/a and $(r/a)^2$ terms which occur in the equations for ψ given on page 43; p, d and f orbitals differ in this respect from s orbitals which, as shown in Fig. 5, have a high electron density at, and near to, the nucleus. Reproduced with permission from *Atoms and Molecules* by M. Karplus and R. N. Porter, copyright 1970 Benjamin/Cummings Publishing Co., Inc.

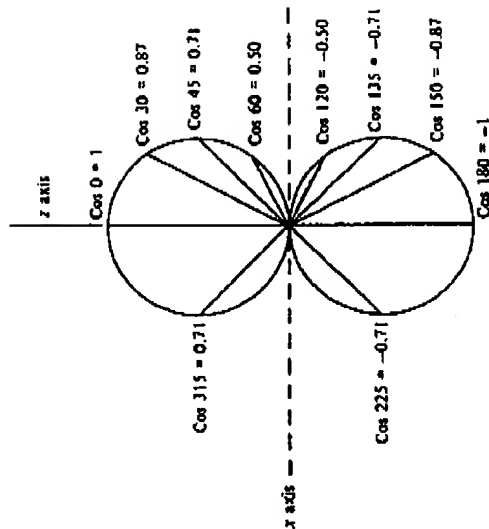


Fig. 8(b).—As stated in the text, the angular part of the wavefunction for a $2p_z$ orbital is $\cos \theta$. One way of plotting $\cos \theta$ is to draw, in the xz or yz plane, a series of lines from the origin (i.e. the nucleus) making an angle θ to the z axis and of length $\cos \theta$ (in centimetres or inches). Joining the extremities of an infinite number of such lines gives two tangential circles (touching at the nucleus). When this is repeated for all possible planes containing the z axis (more easily done by rotating this diagram about the z axis), the resulting shape is two spheres in contact.

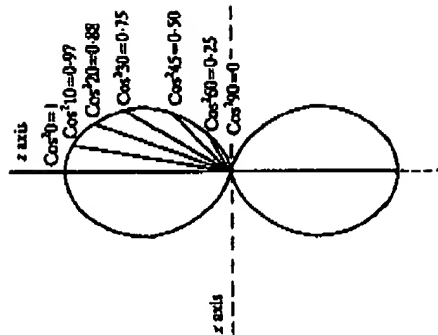


Fig. 8(c).—Some books show diagrams of 2p orbitals as 'figures-of-eight'. These represent $A^2(\theta, \phi)$, which for $2p_z$ is simply $\cos^2 \theta$; this function can be drawn in the same way as was done for $A(\theta, \phi)$ but ignoring that $\cos^2 \theta$ is positive in all four quadrants.

Fig. 8(d).—Contour diagram of constant ψ^2 for 2p, 3p and 3d orbitals. It is impossible to plot in three dimensions the variation of the four variables $\psi(\theta, \phi, r)$, r , θ and ϕ . This difficulty can be overcome to a large degree by holding $\psi(\theta, \phi, r)$ constant and plotting the spatial variations of $\psi^2(\theta, \phi, r)$, which in two dimensions results in a contour map of the electron density within

The periodic table

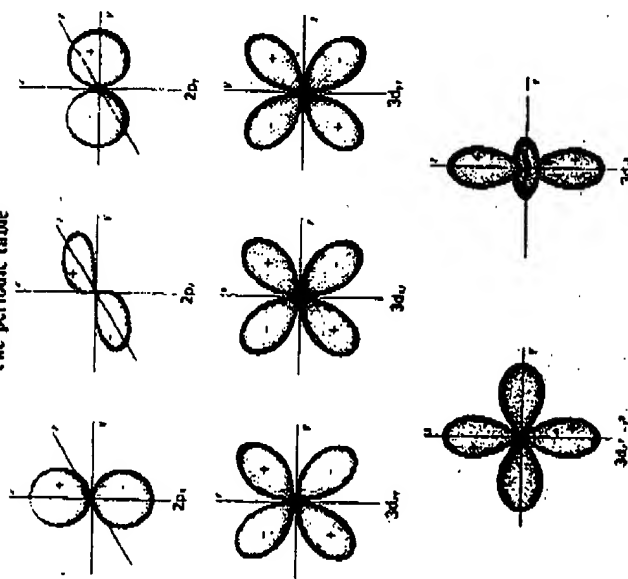
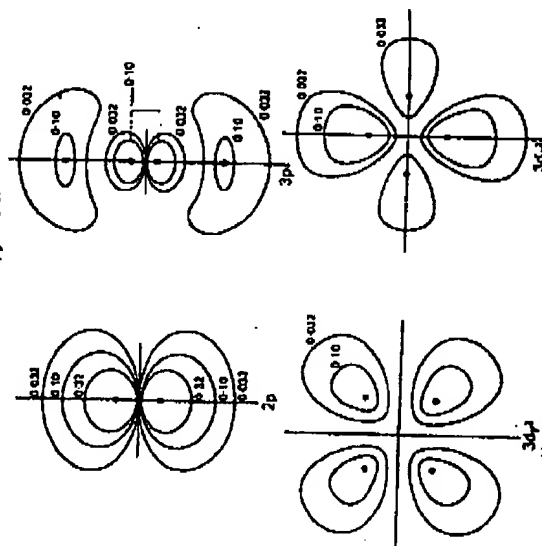


Fig. 8(d) — The angular part of the wavefunction, $A(\theta, \phi)$, for the 2p and 3d orbitals of the hydrogen atom. Note the convention for denoting the different p orbitals and d orbitals which differ in their orientation relative to the axes x , y and z .



the orbital. It is to be realized that in three dimensions the contours shown above become contour surfaces. The figures represent the ratio ψ/ψ_{max} ; the dots show the positions of maximum electron density in each part of the orbitals.

p and d orbitals

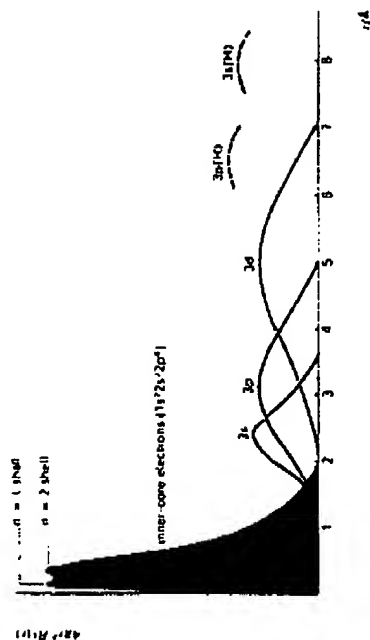


Fig. 9 — Radial electron density functions for the sodium atom, showing the contraction effect of orbital penetration on the 3s, 3p and 3d orbitals. The position of the maximum for radial electron density functions of hydrogen 1s and 2p orbitals is indicated by the broken curves labelled 1s(H) and 2p(H). The hydrogen 3d orbital is similar in position to that shown for sodium.

are occupied; it is interesting to see the effect of orbital penetration on the outer 3s, 3p and 3d orbitals in such an atom (Fig. 9). Without the effect of orbital penetration it would be expected that the electron in sodium's $n = 3$ quantum shell would experience the attraction of the nuclear charge (+11) moderated by the ten electrons in the $n = 1$ and $n = 2$ shells, which are between it and the nucleus (remembering that the electrons having the highest value of the principal quantum number are farthest out from the nucleus). The ten inner-shell electrons will repel the outermost electron, which is equivalent to reducing the attractive force of the nucleus: the $n = 3$ electron is said to be shielded from the full nuclear charge by the inner electrons. The effective nuclear charge felt by the $n = 3$ electron might then be expected to equal +1 (i.e. $11 - 10$), in which case the radial distribution functions would appear as in Fig. 7, the 3d, 3p and 3s orbitals having their maximum 'humps' at about 4.5, 6 and 6.5 Å from the nucleus respectively. In sodium the 3d orbital certainly has its hump at 4.5 Å from the nucleus, but the 3s and 3p orbitals have their maxima very much closer than expected. This is because the 3s and 3p orbitals penetrate close in to the nucleus through the inner-shell electrons and therefore experience a nuclear charge considerably greater than +1; the effect is more marked for s orbitals, as mentioned above when discussing Fig. 7. Hence a 3s electron in the sodium atom would experience a higher effective charge than would a 3p electron. The 3d orbital shows no penetration effect, and an electron in such an orbital, well outside the inner shell of ten electrons, would experience an effective nuclear charge of about +1.

Because of this penetration effect*, a 3s electron in the sodium atom is more strongly bound than a 3p electron, which in turn is more strongly bound than a 3d electron. The overall result of penetration on the sequence of orbital energies for the first two dozen or so elements in the periodic table is shown in Fig. 4. As is obvious from the

* Note that although the penetration effect increases the attraction between an electron and the nucleus there will also be an increase in repulsion between this electron and the other electrons as they come closer together. It so happens that the attractive energy gained by penetrating outweighs this repulsion.

The periodic table

radial distribution functions for 3s, 3p and 3d orbitals in Fig. 9, the *smallest orbitals are those which are the most strongly bound to the nucleus*.

Using the sequence of orbital energies given in Fig. 4 and Pauli's exclusion principle, we can now begin to build up the periodic table of the elements. We shall use the notation ↑ to mean a single electron (with, say, spin +½) and ↑↓ to mean two electrons occupying the same orbital with their spins paired (i.e. spins +½ and -½).

THE HYDROGEN ATOM

The solution of the Schrödinger wave equation for a one-electron system (e.g. H, He⁺, Li²⁺) gives the energy of the electron as

$$E = -\frac{2\pi^2 me^4 Z^2}{h^2} \times \frac{1}{n^2}$$

where e is the electronic charge, Z is the nuclear charge and n is the principal quantum number. For hydrogen, $Z = 1$ and hence

$$E = -1310 \times \frac{1}{n^2} \text{ kJ (mol H)}^{-1}$$

Fig. 10 illustrates the ground state configuration of the hydrogen atom. When two electrons are placed in the 1s orbital, as in the hydride ion H⁻, they repel one another so strongly that the binding energy of the electrons falls from -1310 kJ to about -63 kJ. From this it can be recognized that the repulsion energy between the two 1s electrons in H⁻ must be 1310 - 63 = 1247 kJ. Since the electrons are much less strongly bound to the nucleus in H⁻ than in H owing to their mutual repulsion, it follows that the hydride ion is considerably larger (radius ≈ 1.5 Å) than the hydrogen atom (radius 0.53 Å).

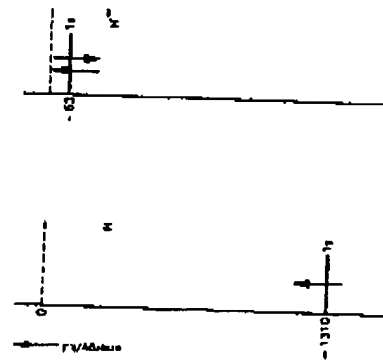


Fig. 10(a) — The electronic structures of the hydrogen atom and the gaseous hydride ion in their ground state (i.e. $n = 1$).

The first short period: lithium to neon

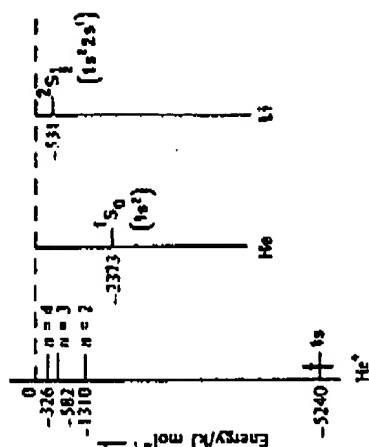


Fig. 10(b) — Energy level diagrams for He⁺, He and Li. Energy level diagrams showing orbitals are only strictly correct for one-electron systems like H and He⁺; in multi-electron species the term symbol corresponding to a given electronic configuration should be used. Thus the singlet ground state of He (symbol ¹S₀) arises from the 1s² configuration and lies 2373 kJ mol⁻¹ below the state corresponding to He⁺ and an isolated electron (i.e. 2373 kJ mol⁻¹ is the first ionization energy of helium). The energy of the helium atomic 1s orbital is presumably -5240 kJ mol⁻¹ but strong repulsion between the two 1s electrons markedly destabilizes the atom and makes it relatively easy to lose the first electron.

The 2s electron of Li is shielded (repelled) by the inner 1s² pair from the full attraction of the nuclear charge; it is also further away from the nucleus, on average, than 1s electrons. Both these effects result in a low first ionization energy of 520 kJ mol⁻¹.

THE HELIUM ATOM

The binding energy of the electron in He⁺ is four times that in the hydrogen atom because of the increased nuclear charge ($Z = 2$): 1310×2^2 or 5240 kJ (mol He⁺)⁻¹. This results in a greatly reduced size of the 1s orbital in He⁺ compared to the hydrogen 1s orbital. The energy required to remove one electron from the helium atom (i.e. the first ionization energy of He) is 2373 kJ, which means that the repulsion energy between the two 1s electrons is 5240 - 2373 or 2867 kJ mol⁻¹; an enormous amount of energy when we are used to thinking of electrons which are spin-paired in the same orbital as constituting a 'stable' system; note that the reduced orbital size increases the electron repulsion energy in He relative to H⁺. It is possible to calculate the total electron binding energy for the 1s² state of helium as 5240 + 1310 or 6550 kJ mol⁻¹ if electron repulsion effects are ignored compared with the value 2373 + 5240 or 7613 kJ mol⁻¹ measured for the 1s² state. It is clearly much more favourable to pair the electrons in the 1s orbital and lose a considerable amount of repulsion energy than to place the second electron in the next available orbital. This calculation illustrates the *Aufbau* (or building-up) principle used to decide into which orbitals the available electrons are to be placed; the occupied orbitals are those which give rise to the most stable state (called the *ground state*) of the atom.

THE FIRST SHORT PERIOD: LITHIUM TO NEON

There is only one orbital in the $n = 1$ quantum shell — $1s$, from Pauli's exclusion principle, we know that a maximum of two electrons, $\uparrow\downarrow$, be accommodated in it.

Hence this quantum shell is completed at helium. The next element, lithium, contains three electrons, and from Fig. 4 it is obvious that the third electron must occupy the 2s orbital since this is the most stable orbital (the one with the most negative energy) after the completed $n = 1$ shell. The electron configuration of lithium in its ground state is therefore $1s^2 2s^1$. The outer 2s electron is relatively easily lost as shown by the low ionization energy of 511 kJ mol^{-1} , which is less than half that of hydrogen. This occurs because although the nuclear charge is $+3$ for lithium, the two 1s electrons shield the 2s electron from the full attraction of the nucleus, resulting in an effective nuclear charge experienced by the 2s electron of only about $+1$; the fact that a 2s electron is further from the nucleus reduces its binding energy still more relative to one in a hydrogen 1s orbital. Lithium therefore readily forms salts containing the Li^+ ion.

Beryllium has the electronic structure $1s^2 2s^2$ because this is 264 kJ mol^{-1} more stable than the configuration $1s^2 2s^1 2p^1$, notwithstanding the considerable repulsion energy which arises by having two electrons in the 2s orbital. It is interesting to compare the $1s^2 2s^2 \rightarrow 1s^2 2s^1 2p^1$ promotion energy for beryllium (264 kJ) with the huge $1s^2 \rightarrow 1s^1 2s^1$ promotion energy for helium (1913 kJ) where the electron has to be promoted to another quantum shell (involving a change in the principal quantum number). Thus although helium cannot be expected to form divalent compounds, the $s \rightarrow p$ promotion for beryllium (involving only a change in l , the secondary quantum number) is relatively easy and beryllium forms many covalent compounds in which the beryllium atom has its orbitals sp , sp^2 or sp^3 hybridized. The first (900 kJ) and second (1756 kJ) ionization energies of beryllium are apparently much too high to allow any salts containing the bare Be^{2+} ion to form.

Boron has five electrons and in the ground state adopts the configuration $1s^2 2s^2 2p^1$ since the 2p orbital is lowest in energy after the 2s. At carbon, which has six electrons, there is something of a dilemma. From Fig. 4 it is obvious that the ground state must be $1s^2 2s^1 2p^2$, but this can represent the configuration of several different energy states, e.g. $1s^1 2s^1 2p^1 2p^1$, $1s^1 2s^1 2p^1 2p^1$ or $1s^1 2s^1 2p^1 2p^1$; guidance on deciding the ground state configuration in such cases is given by the following rules:

- Electrons avoid being spin-paired in the same orbital as far as possible to reduce their Coulombic repulsion; the extent of this repulsion varies with the size of the orbital. Two electrons confined to the small 1s orbital of Be^{2+} (isoelectronic with helium) repel each other to the extent of 6157 kJ mol^{-1} , but this falls to about 120 kJ mol^{-1} for two paired electrons in a larger carbon 2p orbital.
- When unpaired electrons occupy degenerate orbitals, the energy of the system is lowest when their spins are parallel (Hund's rule of maximum multiplicity). This is due to a quantum mechanical phenomenon, called the exchange energy, which has no classical counterpart in our macroscopic world. Tiny spinning particles such as electrons and neutrons tend to avoid occupying similar regions of space when their spins are parallel; for electrons this will obviously result in a lowering of electrostatic repulsion. The effect can be surprisingly large, as shown by the difference of 77 kJ mol^{-1} which exists between the $1s^1 2s^1$ and $1s^1 2s^1$ configurations of helium.

From these rules it can be deduced that a carbon atom in its ground state has the electron configuration $1s^2 2s^2 2p^2$. The energy required to promote carbon to the

configuration $1s^2 2s^1 2p^1 2p^1$ is reasonably low ($403.7 \text{ kJ mol}^{-1}$) and results in the formation of CX_4 being energetically more favourable than the formation of CX_2 ; hence carbon is almost always four-covalent in its compounds (see page 208).

The electronic configurations of the remaining elements in the first short period are built up following the rules used above:

N	$1s^2 2s^2 2p^1 2p^1 2p^1$
O	$1s^2 2s^2 2p^1 2p^1 2p^1$
F	$1s^2 2s^2 2p^1 2p^1 2p^1$
Ne	$1s^2 2s^2 2p^1 2p^1 2p^1$

Although in theory these last four elements might increase their usual valencies via promotion of an electron to the empty 3s orbital, the energy required for this (between 800 and 1600 kJ, depending on the element) is prohibitively large and the covalency maxima remain 3, 2, 1 and 0 for nitrogen, oxygen, fluorine and neon respectively.

The apparently erratic variation in first ionization energies across the $n = 2$ quantum shell from lithium to neon (Fig. 11(b)) is explicable in terms of the electronic configurations given above for these elements. The value for beryllium is higher than that for lithium because the increase in nuclear charge more than compensates for

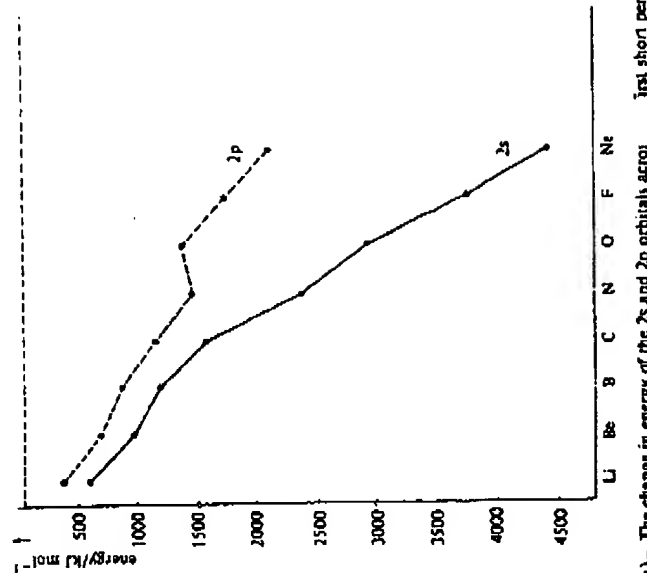


Fig. 11(a).—The change in energy of the 2s and 2p orbitals across the first short period.

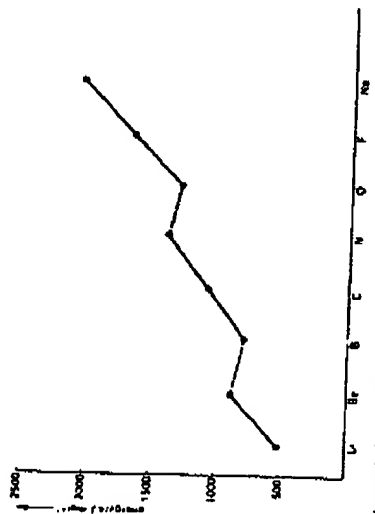


Fig. 11(b) — The variation in first ionization energies from lithium to neon.

the electronic repulsions between the two 2s electrons of beryllium. At boron, configuration $1s^2 2s^2 2p^1$, the least strongly bound electron is now in a 2p orbital, and since 2p orbitals are not stabilized by penetration effects to the same extent as 2s orbitals, the ionization energy of boron is lower than expected by extrapolation from lithium ($1s^2 2s^1$) and beryllium ($1s^2 2s^2$). The ionization energies rise smoothly between boron and nitrogen as one electron is placed successively in each of the three 2p orbitals. As shown in Fig. 8, the p orbitals are orientated at right angles to each other, and because of this p electrons do not shield each other very effectively from the Coulombic attraction of the nucleus; therefore the increase in nuclear charge from boron to nitrogen means that the 2p electrons become more and more strongly bound and this is reflected in the increasing ionization energies. The drop in ionization energy between nitrogen and oxygen occurs because from oxygen to neon the electrons in the 2p orbitals are being paired up, which results in a repulsion term not present for boron, carbon and nitrogen. The increased nuclear charge, penetration effects and shielding combine to make the first ionization energy of neon about four times larger than that of lithium, thus precluding the formation of ionic salts of neon containing the cation Ne^+ . Similarly, derivatives of F^+ are highly unlikely. The above three effects fall off somewhat with increasing atomic number down a particular group; among the halogens, the ionization energy falls steadily until at iodine it is only 1009 kJ, and a few derivatives of I^+ have been isolated.

Figure 11(a) represents the change in 2s and 2p orbital energies from lithium to neon; note the similarities to Fig. 11(b). The difference between the 2s and 2p energies for a given atom gives the magnitude of the 2s orbital penetration effect, which even at lithium amounts to 175.7 kJ. As the 2s orbital becomes more strongly bound to the nucleus more effectively from the full attraction of the nucleus; hence the divergence of the 2s and 2p orbital energies, especially at oxygen, fluorine and neon, where electronic repulsions cause further destabilization of the 2p orbitals. The 2s-2p separation, being very sensitive to the increasing nuclear charge, rises to 3000 kJ at sodium and a stage 16000 kJ at copper.

THE SECOND SHORT PERIOD: SODIUM TO ARGON

At neon the $n = 2$ quantum shell is completed, so that the next element, sodium, has its last electron placed in the lowest-energy orbital of the $n = 3$ shell, the 3s, giving sodium the electronic configuration $1s^2 2s^2 2p^6 3s^1$. The next seven elements complete the 3s and 3p orbitals in a regular manner following the rules adopted for the $n = 2$ shell:

Na	$1s^2 2s^2 2p^6 3s^1$
Mg	$1s^2 2s^2 2p^6 3s^2$
Al	$1s^2 2s^2 2p^6 3s^2 3p^1$
Si	$1s^2 2s^2 2p^6 3s^2 3p^2$
P	$1s^2 2s^2 2p^6 3s^2 3p^3$
S	$1s^2 2s^2 2p^6 3s^2 3p^4$
Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$
Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$

THE FIRST LONG PERIOD

Potassium has one more electron than argon and one might predict that, because the 4s orbital is less stable than the 3d set (Figure 4), this electron would be found in one of the five degenerate 3d orbitals giving potassium the configuration $[Ar] 3d^1$. However, the effects of penetration and inter-electron repulsions *within the atom as a whole* are such that the ground state of potassium is that in which the 4s orbital is occupied: $1s^2 2s^2 2p^6 3s^2 3p^4$. The ground state turns out to be about 255 kJ mol⁻¹ more stable than the excited state with the $[Ar] 3d^1$ configuration. A 4s and a 3d orbital are of approximately the same size at this position in the periodic table so that electrons in 4s orbitals do not shield 3d electrons very effectively from the attraction of the nucleus. At calcium, the increase in nuclear charge and the poor shielding effect of a single 4s electron make the 3d orbitals more stable than they were at potassium; however, the calcium atom is most stable when the twentieth electron is accommodated in the 4s orbital giving the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$.

It is only at the next element, scandium, that the 3d orbitals start to fill giving scandium the configuration $[Ar] 3d^1 4s^2$. Although there is room for ten electrons in the 3d orbitals it will be noticed that two of scandium's electrons are placed in the less stable 4s orbital. This situation arises because the ground state of scandium hinges on a subtle balance of penetration, inter-electron repulsions and poor mutual 3d-4s shielding which can only be achieved if the 4s orbital is fully occupied. When the three outer electrons of scandium are all placed in 3d orbitals it is found that the resulting $[Ar] 3d^3$ configuration represents an excited state some 400 kJ above the ground state. This illustrates an important point: the outer electrons in some atoms are not necessarily placed in orbitals having the lowest energy. The actual orbitals occupied are always those which result in the lowest energy for the atom as a whole and this depends on several factors only one of which is the orbital energy. However, such a situation can only occur when the two sets of orbitals in question (for example, the 3d and 4s orbitals) are of similar energy. On ionization of the first row transition metals the first two electrons come from the *least stable* orbital which

The periodic table

is the 4s and hence their M^{2+} and M^{3+} ions always have $3d^n$ configurations. The influence of an increased effective nuclear charge on the very delicate balance of factors affecting the $3d$ 4s occupancy can be judged from the ground state electron configurations of Sc^+ (isoelectronic with Ca) and Sc^{2+} (isoelectronic with K) which are $[Ar]3d^14s^1$ and $[Ar]3d^1$ respectively. In this region of the periodic table the difference in 4s and 3d orbital energies is approximately proportional to the square of the effective nuclear charge which, for the scandium species, is in the order $Sc^{2+} > Sc^+ > Sc$.

The nine elements after scandium are derived by filling up the five d orbitals. Slight variations from regularity occur at Cr ($3d^54s^1$) and Cu ($3d^{10}4s^1$) owing to the similarity of the 3d and 4s orbital energies which allows relatively small effects to dictate the final electron configuration. For example, at chromium where the difference between the $3d^54s^1$ and $3d^44s^2$ configurations amounts to only 90 kJ, it is slightly more favourable to have the electrons occupying orbitals with parallel spins to minimize the effect of both electronic repulsions and the exchange energy. For the second- and third-row transition metals the increased nuclear charge results in the d and s orbitals becoming even closer in energy, and it is then impossible to predict their ground states with certainty using our simple rules (see the periodic table printed on the foldout at the end of the book). These minor variations are of relatively little consequence; much more important to chemists are the metal ions M^{2+} and M^{3+} which invariably have the $d^n s^0$ outer electron configuration.

The $4s^1$ outer configuration of copper and potassium suggests that they might be chemically comparable. However, the poor mutual shielding effect of 3d and 4s electrons is sufficient to make the first ionization energy of copper nearly twice that of potassium. On the other hand, the second ionization energy of copper (where the electron is removed from a 3d orbital) is almost *half* that of potassium (where the second electron comes from a strongly bound 3p orbital). Copper is thus able to have variable valency, commonly occurring as Cu^+ and Cu^{2+} ions. Furthermore, although copper has ten more electrons than potassium, the effect of poor mutual shielding of the filled 3d orbitals in Cu^+ is to make the ion very much smaller than K^+ ($r_{Co} = 0.93$ Å, $r_{K^+} = 1.33$ Å, $r_{Na^+} = 0.95$ Å). Hence there is little similarity in the chemistry of copper on the one hand and that of the alkali metals on the other.

When the 3d orbitals are filled at zinc, the next available orbitals are the three degenerate 4p orbitals, and gallium thus has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$ which places it in Group III below aluminium. The effect of poor shielding by the filled 3d orbitals on the outer 4s and 4p electrons is apparent in the ionization energies (see page 177) of gallium which are almost equal to those of aluminium, showing that the electrons in gallium are much more tightly bound than would be expected by simple extrapolation of the trends in ionization energies noted in Groups I and II (where these energies decrease smoothly down the groups with increasing atomic number of the elements). Continued filling of the 4p orbitals in the normal systematic manner gives the Group IV (germanium), V (arsenic), VI (selenium), VII (bromine) and VIII (krypton) elements, which thus completes the first long period.

THE SECOND LONG PERIOD

The sequence of orbitals in this period closely resembles that of the first long period: the 5s orbital is occupied at rubidium and strontium before the 4d orbitals begin to

Synthesis of elements after uranium and possible extension of the periodic table 55

fill up giving rise to the ten elements of the second transition series. From In to Xe the outer electrons enter the 5p orbitals and build up the next set of main group elements.

THE HEAVY ELEMENTS

In line with all the preceding periods, the 6s orbital now begins to fill at what would have been expected to be the third long period. Thus caesium and barium have the 6s¹ and 6s² outer electron configurations respectively, and with the next element, lanthanum, the series of 5d transition elements apparently begins. However, at this point in the periodic table the combination of penetration effects, shielding effects and increasing nuclear charge significantly stabilizes the 4f orbitals. (At caesium the 4f orbital energy is virtually identical to that of the 4f orbitals in hydrogen, so efficiently are the f orbitals shielded by the inner electrons.) These effects drop the 4f orbital energy at cerium to a level below that of the 5d and 6p orbitals, and hence cerium has the outer configuration $4f^2 5s^2 5p^6 6s^2$; continued filling up of the f orbitals in a more or less straightforward fashion gives rise to the fourteen lanthanide elements. When the 4f orbitals are full, the third d transition series is completed by the filling of the 5d orbitals, which are still lower in energy than the 6p orbitals.

Therefore the next non-transition element after barium occurs twenty-five places further on in the periodic table as the 6p orbitals begin to be occupied at thallium. The ionization energies of thallium (see page 177) are higher than expected by extrapolation from either indium or strontium owing to the poor shielding properties of both the 5d and 4f electrons (which cause the outer $6s^2 6p^1$ electrons to be strongly bound to the nucleus). The combination of high ionization energies and low $Tl-X$ bond energies (bond energies normally decrease down a group owing to the size and diffuseness of orbitals increasing with atomic number, which leads to poor orbital overlap) makes thallium reluctant to form either Tl^{3+} ions or TlX_3 covalent derivatives; more often it exists as the thallium(I) ion Tl^+ which has a $4f^{14} 5d^{10} 6s^2$ configuration. The chemistry of thallium in the monovalent state is similar to that of the heavier alkali metals (e.g. many of their salts are isomorphous), although solubilities (e.g. of the halides) closely resemble those of the corresponding silver salts. This tendency not to use the tightly bound ns^2 outer electrons is also marked with lead and bismuth, and was becoming apparent even at indium and tin in the previous period (where it was due to the poor shielding of the 4d electrons).

Predictably, after the 6p orbitals have been filled at radon the next two elements, francium and radium, have the outer configurations 7s¹ and 7s². However, the similar energies of 6d and 5f orbitals after actinium ($6d^1 7s^2$) result in several irregular electron arrangements among the remaining elements. Although the IUPAC ordering of the groups into A and B subsections is used in this book, there is a growing tendency to adopt a newly proposed system in which the periodic table is divided into eighteen groups starting with the alkali metals as Group 1 and ending with the rare gases in Group 18; Group IIIB (B, Al, Ga, In, Tl) would then become Group 13 because of the intervening transition metals in Groups 3–12.

SYNTHESIS OF ELEMENTS AFTER URANIUM AND POSSIBLE EXTENSION OF THE PERIODIC TABLE

Bismuth is the last element in the periodic table to have a stable isotope so that all

Chapter 6

Group III. Boron, Aluminium, Gallium, Indium and Thallium

INTRODUCTION

Among the Group I and II elements the ionization energies were found to decrease with increasing atomic number; this is not the case in Group III, where the ionization energies vary down the group in an apparently erratic way (Table 26 and Fig. 50). On closer inspection, however, it is seen that the inner electronic configurations of the Group III elements are not identical; instead of a rare gas electron structure between them and the nucleus, the ns^2np^1 electrons of gallium, indium and thallium are outside a filled set of $(n-1)d$ orbitals and have what might be called a 'd¹⁰ core'. The inner electron structure of thallium also contains fourteen electrons in the 4f orbitals filled during the building up of the preceding lanthanide series of elements.

The increasing effective nuclear charge and size contraction, which occur during the filling of d and f orbitals (see Chapter 1), combine to make the outer s and p electrons of Ga, In and Tl more strongly held than would be expected by simple extrapolation from boron and aluminium. The drop in ionization energies between Ga and In mainly reflects the fact that both elements have an identical inner electron core and hence there is an expected decrease in electron binding at indium because its outer electrons are further from the nucleus. There is also an increase in effective nuclear charge when progressing from left to right across any given period and this is responsible (together with the above 'core effects') for the observed variation in first ionization energies which are in the order Group I < Group II < Group III.

TRIVALENT CATIONS

The M^{3+} state for gallium, indium and thallium will be energetically less favourable than Al^{3+} because the high ionization energies of these three elements cannot always

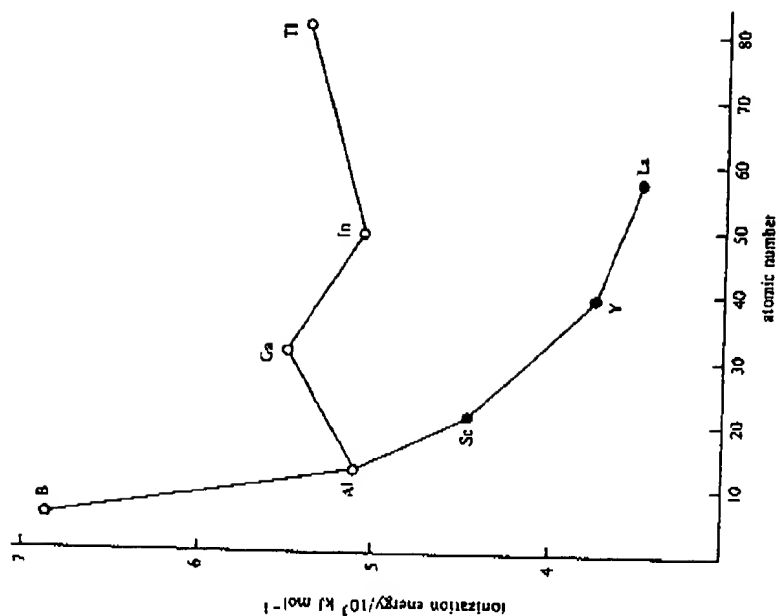


Fig. 50—The sum of the first three ionization energies plotted against atomic number for the Group IIIA (Sc, Y, La) and Group IIIB (B, Al, Ga, In, Tl) elements. The effect of the d^{10} and f^{14} inner electron cores on the ionization energies of the Group IIIB elements is strikingly apparent (the Group IIIA elements all have s^2p^1 cores).

be balanced by the lattice energies of possible reaction products (the lattice energies decrease down the aluminium, gallium, indium and thallium group owing to the increasing size of the M^{3+} cations) and, for the group as a whole, the M^{3+} state is the exception and not the rule. In fact, of the trihalides only the high-melting fluorides of Al, Ga, In and Tl are usually considered to be ionic. More commonly these elements achieve an oxidation state of three by forming covalent compounds via $ns \rightarrow sp$ promotion.

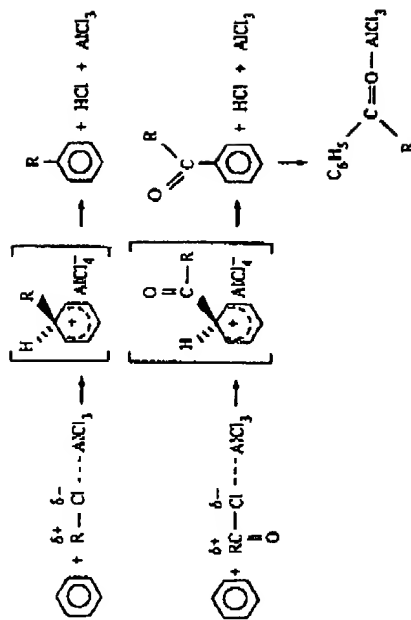
Although simple M^{3+} cations are uncommon in anhydrous compounds of Group III elements, the hydrated ions of aluminium, gallium, indium and thallium are well known in aqueous solution. Nuclear magnetic resonance studies show that there are six water molecules held strongly by these ions in their primary coordination spheres and there is undoubtedly a layer of further solvent hydrogen-bonded to these hexahydrated species. At high salt concentration, ion association occurs and, for

Table 26—The Group III elements

Element	Atomic number	1st IE (kJ mol^{-1})	2nd IE (kJ mol^{-1})	3rd IE (kJ mol^{-1})	4th IE (kJ mol^{-1})	Radius of M^{3+} (Å)
Boron, B	5	800.3	2427	3658	25030	—
Aluminium, Al	13	564.2	1816	2744	11580	—
Gallium, Ga	31	564.2	1979	2962	6193	—
Indium, In	49	558.3	1820	2705	5230	—
Thallium, Tl	81	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	589.0	1970	2975	1.64
		[Kr] 4d ¹⁰ 5s ² 5p ¹			4896	—
		[Ar] 3d ¹⁰ 4s ² 4p ¹			5230	—
		[Ne] 3s ² 3p ¹			6193	—
					11580	—
					25030	—
					—	0.68
						0.76
						0.94
						1.03

FRIEDEL-CRAFTS CATALYSIS

Aluminium halides, particularly AlCl_3 , are widely used in organic chemistry as catalysts in the Friedel-Crafts alkylation or acylation of aromatic compounds. They behave as Lewis acids by strongly polarizing the attacking organic halide to form an $\text{R}^{\delta+} \cdots \text{X}^{\delta-} \cdots \text{AlX}_3$ intermediate in the reaction:



With some tertiary alkyl halides and many acyl chlorides the polarization may be so extreme that the attacking species is essentially a 'free' carbonium ion, R^+ . Beryllium, boron and gallium halides are also able to function in this way as Friedel-Crafts catalysts.

OCCURRENCE OF THE GROUP III ELEMENTS

Boron

About 3 ppm of the Earth's crust; main sources are the sodium borates $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{B}_6\text{O}_{11} \cdot 10\text{H}_2\text{O}$.

Aluminium

7.5%; the most common of all metals; the most commercially important ore is the hydrated oxide, bauxite, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Gallium

15 ppm; widely distributed in nature but only in minute concentrations; zinc blende ZnS often contains 0.1%–0.5% gallium.

Indium

0.1 ppm; no concentrated deposits have been found and, like gallium, it is obtained from the residues of zinc and lead smelting processes.

Thallium

0.3 ppm; obtained from the flue dust of sulphuric acid works.

EXTRACTION

Boron

Amorphous boron of about 95% purity is obtained by reducing boric oxide with either sodium or magnesium:



Pure, crystalline boron can be obtained in gram quantities by passing a hydrogen-boron trihalide mixture over a tantalum wire held at 1100–1300°C.

Aluminium

Bauxite is purified by dissolving it in sodium hydroxide solution (to give sodium aluminate), when the oxides of iron present precipitate out. If the solution is held at 25–35°C and a little $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ added to it, most of the bauxite present crystallizes out as the trihydrate; this is heated to 1200°C, dissolved in molten cryolite, Na_3AlF_6 , and electrolysed between carbon electrodes at 960–980°C.

Gallium, indium and thallium

As mentioned above, these metals are obtained as by-products in the production of zinc, lead and sulphuric acid. Gallium may be purified by electrolysis of an alkaline solution of one of its salts (gallium hydroxide is amphoteric and dissolves in alkali to give gallates).

THE ELEMENTS

The melting points within this group of elements vary widely: boron, ~2300°C; aluminium, 639°C; gallium, 29.6°C; indium, 156°C; thallium, 302.5°C. Gallium, with a boiling point of about 2030°C, has the longest liquid range of all the elements and has been used in high-temperature thermometers.

Boron is notable for the complexity of its crystalline forms, all of which are based

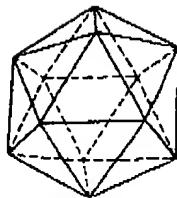


Fig. 53... An icosahedron has twenty equilateral (triangular) faces and a total of twelve vertices. The icosahedral B_{12} units is the basic 'building block' in the three known forms of crystalline boron.

on icosahedra of boron atoms; for example, the α rhombohedral modification consists of an approximately cubic close-packed arrangement of icosahedral B_{12} groups bound to each other by covalent bonds (Fig. 53). Aluminium has a face-centred cubic structure, but there is some evidence to suggest that all three outer electrons on the aluminium atoms are not used in bonding, which would account for the comparatively low melting point (only 8°C above that of magnesium). Gallium has a complex structure in which the atoms have the following set of neighbours: one at 2.44 \AA , two at 2.70 \AA , two at 2.73 \AA and two at 2.79 \AA . It is thought that gallium may also contain some pairs of atoms in the liquid state because the X-ray diffraction pattern is different from that of a simple liquid like mercury. Indium has a slightly distorted face-centred cubic structure. Thallium is dimorphic, having hexagonal (α) and cubic (β) forms.

Elemental boron is highly inert and is not affected by acids, even boiling hydrofluoric; fused sodium hydroxide slowly attacks it but only above 500°C . By contrast, the other elements are quite reactive and dissolve readily in acids giving salts, and aluminium, gallium and indium, being amphoteric, dissolve in alkalis evolving hydrogen and forming aluminates, gallates and indates.

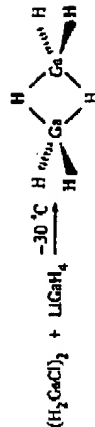
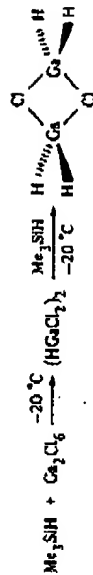
COMPOUNDS OF THE GROUP III ELEMENTS

Hydrides

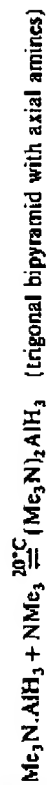
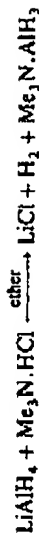
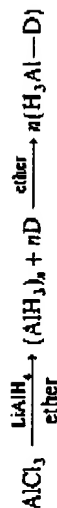
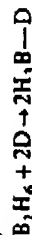
(See Chapter 2 for a discussion of the hydrides of boron.) The expected monomeric hydrides of this group, MH_3 , are unstable and can only be detected at low pressures where the polymerization rate is slow. For example, when aluminium is slowly vaporized off a tungsten filament in a current of hydrogen, the formation of AlH_3 is revealed by mass spectral analysis; if the amount of AlH_3 in the vapour phase is increased (by evaporating the aluminium metal more quickly) then the dimer Al_2H_6 can also be detected. Under similar conditions the much less thermally stable GaH_3 and InH_3 can be produced, but there was no indication of dimer formation. However, digallane has been isolated very faintly as a volatile species which decomposes above

Compounds of the group III elements

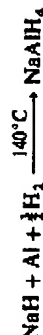
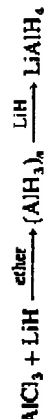
-10°C into gallium metal and hydrogen:



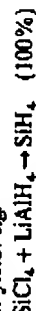
Although the free monomeric hydrides of Group III do not exist under normal conditions, their complexes with suitable donor molecules, such as amines, are well known: e.g.



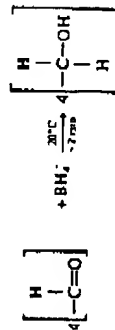
The donor species D can also be the hydride ion H^- , in which case the reaction product is the tetrahedral anion MH_4^- :



Lithium tetrahydroaluminate is a useful reducing agent and, for example, reacts with many covalent metal and metalloidal halides to give the corresponding hydrides, often in high yield: e.g.



Sodium tetrahydroborate, $NaBH_4$, which is soluble in water and a variety of organic solvents, readily reduces aldehydes to primary alcohols:



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the high-velocity outflow of gas, strong nonthermal emission (implying relativistic particles and magnetic intense and often polarized and highly variable radiation in optical, ultraviolet, and x-ray wavelengths, and ejection of relativistic material. In the most extreme cases (quasars and N galaxies) the energy in the nuclear activity is that in the rest of the galaxy combined. The ultimate nature of this activity, whether in some extreme stellar population or some previously unobserved type of object (for example, black holes) remains completely unknown. There are astronomers who suspect that active galactic nuclei are the even more extreme, but in many ways similar, phenomenon of quasistellar objects. See BLACKHOLE; QUASAR. The nearest galaxies to the Milky Way Galaxy are the Large and Small Magellanic Clouds, two small irregulars lying about 180,000 light-years away. The nearest bright galaxy is the Andromeda Nebula, M31, visible to the naked eye in the constellation of the same name. It is at a distance of almost 2×10^6 light-years. These galaxies and a handful of fainter ones (a few million light-years) make up the Local Group, of which the Milky Way Galaxy is a member. See ANDROMEDA GALAXY; MAGELLANIC CLOUDS.

(E.L.T.; J.B.T.)

A mineral with composition PbS (lead sulfide) and to the rock salt (NaCl) structure type. Galena usually occurs in cubes, sometimes modified by the octahedral form, with cubic cleavage, brilliant metallic luster, color lead gray, specific gravity 7.5, and hardness $2\frac{1}{2}$ on Mohs scale.

It is widely distributed and constitutes by far the most important ore for lead. Silver, antimony, arsenic, copper, and bismuth often occur in intimate association with galena; many of these elements are mined for lead also include many other products. Important localities include Broken Hill, New South Wales, the tri-state district of Missouri, Kansas, and Oklahoma, and numerous occurrences in Colorado, Montana, and Idaho.

(P.B.M.)

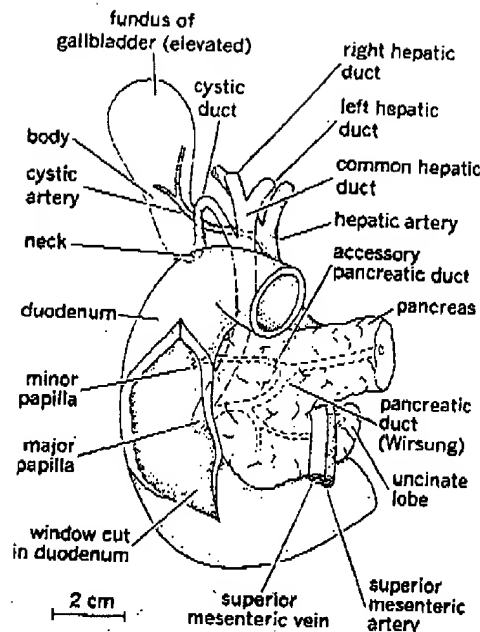
Transformations The family of mathematical transformations used in newtonian mechanics to relate the coordinates of uniformly moving (inertial) reference frames, moving along their common (x, x') direction. Transformation equations can be put in the form of Lorentz equations, where x, y, z and x', y', z' are the coordinates of a given particle, and v is the speed of one frame relative to the other. See FRAME OF REFERENCE.

(E.L.H.)

A hollow muscular organ, present in humans and other mammals, which receives dilute bile from the liver, stores it, and discharges it into the duodenum. Although the gallbladder is of great importance in humans because it regulates biliary tract pressures, and, when discharging, precipitates various constituents of the bile. See CHOLECYSTITIS; GALLSTONES.

The network of bile ducts lying outside the liver is known as the extrahepatic biliary tract. In humans (see illustration) right and left hepatic ducts empty into the common hepatic duct, which joins the duodenum as the common bile duct, or choledochus. The gallbladder and cystic duct thus function as accessory organs and therefore are removable. The gallbladder is converted into main-line structures by the sphincter at the choledochoduodenal junction. Contraction of this sphincter between meals forces the bile into the gallbladder. See LIVER.

The evacuation of the gallbladder is accomplished by a mechanism which is set off by the presence of fatty acids and hydrogogue cathartics in the duodenum and



Extrahepatic biliary tract in humans.

upper jejunum. Absorption of these substances by the mucous membrane results in the release of cholecystokinin, a hormone which rapidly circulates in the bloodstream and simultaneously produces contraction of the gallbladder and relaxation of the sphincter of Oddi. The most effective food is egg yolk which contains certain L-amino acids.

(E.A.B.)

Galliformes The order of birds of great economic significance because it includes important domestic and game birds. Seven families of living Galliformes are usually recognized: Megapodiidae (mound birds and brush turkeys), Cracidae (chachalacas, guans, and curassows), Tetraonidae (grouse), Phasianidae (pheasants, partridge, and quail), Numididae (guinea fowl), Meleagrididae (turkeys), and Opisthocomidae (hoatzins). See AVES; BIRDS; UPLAND GAME.

(K.C.P.)

Gallium A chemical element, Ga, atomic number 31 and atomic weight 69.72, Gallium was discovered by Lecoq de Boisbaudran in France in 1875. Gallium has a great temperature range in the liquid state, prompting its use to some extent in high-temperature thermometers and manometers. In an

I																0																	
1	2																	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H	He																	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar
																		Transition Elements															
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86																
Cs	Ba	La	M	Te	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118																
Fr	Ra	Ac	Rf	Ha																													

828 Gallstones

Selected physical properties of gallium

Property	Value
Melting point	29.78°C (85.60°F)
Boiling point	2237°C (4059°F)
Hardness, Mohs scale	1.5
Density	
Solid	
at 20°C (68°F)	5.907 g/cm ³
at 29.7°C (85.35°F)	5.9037 g/cm ³
Liquid	
at -25.6°C (-32.1°F)	6.153 ± 0.008 g/cm ³
at -18.5°C (-2.66°F)	6.136 g/cm ³
at 29.8°C (85.65°F)	6.0948 g/cm ³
at 1100°C (2012°F)	5.445 g/cm ³

alloy with silver and tin, gallium helps to form a suitable replacement for amalgam in dental fillings. Gallium is also used to solder nonmetallic materials, including gems, to metals. Gallium arsenide can be used in a system for translating mechanical motion into electrical impulses. Synthetic superconducting articles are prepared by making a porous matrix of vanadium or tantalum and impregnating it with gallium hydride. Gallium has given excellent results in a semiconductor for use in rectifiers, transistors, photoconductors, light sources, laser or maser diodes, and refrigerating devices.

Solid gallium looks bluish gray when exposed to the atmosphere. Liquid gallium is silver white with a bright mirror surface. The freezing point of gallium is lower than that of any metal except mercury (-39°C or -38°F) and cesium (28.5°C or 83.3°F). Some properties of gallium are given in the table.

Gallium is chemically similar to aluminum. It is amphoteric but slightly more acid than aluminum. The normal valence of gallium is 3+, and it forms hydroxides, oxides, and salts. Gallium burns in air when heated to 500°C (930°F). It reacts vigorously with boiling water, but only slightly in water at room temperature. The salts of gallium are colorless; they are prepared directly from the metal, since purification of the metal is simpler than purification of the salts.

Gallium forms low-melting eutectic alloys with several metals, and intermetallic compounds with many others. All aluminum contains small amounts of gallium as a harmless impurity, but intergranular penetration by larger amounts of gallium at 30°C (86°F) causes catastrophic failure on loading. (W.D.W.)

Gallstones Round, oval, or faceted concretions formed within the gallbladder from the salts and pigment of bile. Such stones may also be formed in any of the bile ducts within or outside of the liver, but the incidence there is low compared to the number originating in the gallbladder. The occurrence of gallstones increases with age, and 20-30% of all elderly adults have one or more such stones. They are particularly common in women, blacks, and individuals with diabetes. Usually about the size of a pea or a marble, gallstones may be extremely tiny, or so large that a single stone completely fills the gallbladder. They may be composed solely of calcium, cholesterol, or bilirubin, but usually represent combinations or mixtures of these three ingredients precipitated from supersaturated bile. See CHOLESTEROL; GALLBLADDER.

Although the mechanism and reason for their formation is not clearly understood, the major predisposing factors are prolonged retention of bile in the gallbladder, abnormal composition of the bile (excessive amounts of cholesterol, bilirubin, or calcium), and infection. Passage of a gallstone through the ducts into the duodenum usually produces severe pain, called biliary colic. Lodged in the distal portion of the common bile duct, a stone may obstruct that structure and produce jaundice and finally cirrhosis of the liver. The most frequent complication of gallstones is cholecystitis. (M.R.H.)

Galvanizing The generic term for any of the techniques for applying thin coatings of zinc to iron or finished products to protect the ferrous base from corrosion; more specifically, the hot dipping that is practiced with mild steel sheet and corrugated sheet piling, molten zinc reacts with the steel to form a zinc-iron alloy. For marine use, magnesium is added.

An electrolytic process (also called cold galvanizing or trovalvanizing) is also used for wire, as well as for requiring deep drawing. An alloy layer does not flake off; the smooth electroplated coating does not flake off. See METAL COATINGS.

Galvanomagnetic effects Electrical and magnetic phenomena occurring when a current-carrying conductor is placed in a magnetic field. The galvanomagnetic effects are closely related to the thermomagnetic and thermoelectric effects.

Let the electric current density j be transverse to the magnetic field H , for example, along x . Then the following transverse effects are observed: (1) Hall effect, a transverse field along y . (2) Ettingshausen effect, a temperature change along y . Also the following transverse-longitudinal effects are observed: (3) Transverse magnetoresistance, an anisotropy in resistance along x . (4) Nernst effect, a temperature change along x . See HALL EFFECT; MAGNETORESISTANCE.

Let the electric current density j be along H . The important effect is longitudinal magnetoresistance, an anisotropy in resistance along H .

Galvanometer A device for indicating very small currents. Although the deflection of a galvanometer coil in the moving coil, the voltage in a closed circuit inducing this current is frequently the quantity of interest.

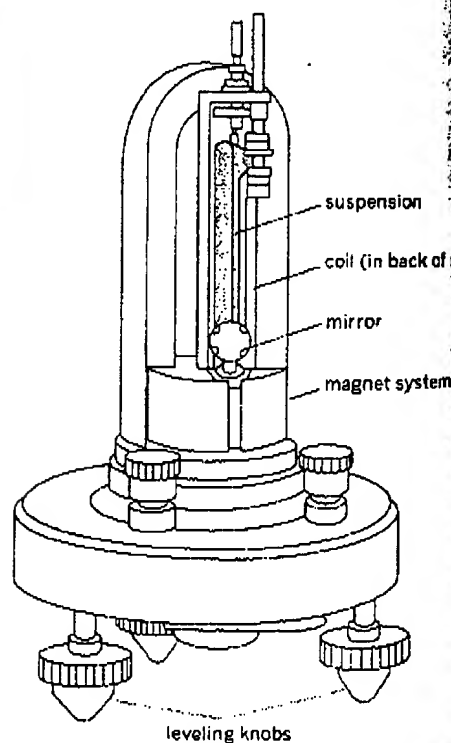
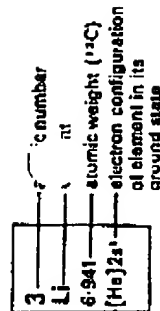


Diagram of light-beam galvanometer. (After D. M. Cox and S. D. Ross, *Process Instruments and Controls Handbook*, 2d ed., McGraw-Hill, 1974)

Periodic Table

emphasizing the differences in electron configurations among the non-transition elements



Group I		Group II		d transition elements										Group V	Group VI	Group VII	Group 0
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008 1s ¹	2 He 4.003 1s ²	3 Li 6.941 [He] 2s ¹	4 Be 9.012 [He] 2s ²	5 B 10.811 [He] 2s ² 2p ¹	6 C 12.011 [He] 2s ² 2p ²	7 N 14.007 [He] 2s ² 2p ³	8 O 15.999 [He] 2s ² 2p ⁴	9 F 18.998 [He] 2s ² 2p ⁵	10 Ne 20.179 [He] 2s ² 2p ⁶	11 Na 22.990 [Ne] 3s ¹	12 Mg 24.306 [Ne] 3s ²	13 Al 26.98 [Ne] 3s ² 3p ¹	14 Si 28.086 [Ne] 3s ² 3p ²	15 P 30.974 [Ne] 3s ² 3p ³	16 S 32.064 [Ne] 3s ² 3p ⁴	17 Cl 35.453 [Ne] 3s ² 3p ⁵	18 Ar 39.948 [Ne] 3s ² 3p ⁶
19 K 39.102 [Ar] 4s ¹	20 Ca 40.08 [Ar] 4s ²	21 Sc 44.956 [Ar] 3d ¹ 4s ²	22 Ti 47.90 [Ar] 3d ² 4s ²	23 V 50.941 [Ar] 3d ³ 4s ²	24 Cr 51.998 [Ar] 3d ⁵ 4s ¹	25 Mn 54.938 [Ar] 3d ⁵ 4s ²	26 Fe 55.847 [Ar] 3d ⁶ 4s ²	27 Co 58.933 [Ar] 3d ⁷ 4s ²	28 Ni 58.71 [Ar] 3d ⁸ 4s ²	29 Cu 63.546 [Ar] 3d ¹⁰ 4s ¹	30 Zn 65.37 [Ar] 3d ¹⁰ 4s ²	31 Ga 69.72 [Ar] 3d ¹⁰ 4s ¹	32 Ge 72.59 [Ar] 3d ¹⁰ 4s ²	33 As 74.922 [Ar] 3d ¹⁰ 4s ²	34 Se 78.96 [Ar] 3d ¹⁰ 4s ²	35 Br 79.904 [Ar] 3d ¹⁰ 4s ²	36 Kr 83.80 [Ar] 3d ¹⁰ 4s ²
37 Rb 85.47 [Kr] 5s ¹	38 Sr 87.62 [Kr] 5s ²	39 Y 88.906 [Kr] 4d ¹ 5s ²	40 Zr 91.22 [Kr] 4d ² 5s ²	41 Nb 92.906 [Kr] 4d ⁴ 5s ¹	42 Mo 95.94 [Kr] 4d ⁵ 5s ¹	43 Tc 98.906 [Kr] 4d ⁵ 5s ²	44 Ru 101.07 [Kr] 4d ⁷ 5s ¹	45 Rh 102.91 [Kr] 4d ⁸ 5s ¹	46 Pd 106.4 [Kr] 4d ¹⁰	47 Ag 107.87 [Kr] 4d ¹⁰ 5s ¹	48 Cd 112.40 [Kr] 4d ¹⁰ 5s ²	49 In 114.82 [Kr] 4d ¹⁰ 5s ²	50 Sn 118.69 [Kr] 4d ¹⁰ 5s ²	51 Sb 121.75 [Kr] 4d ¹⁰ 5s ²	52 Te 127.60 [Kr] 4d ¹⁰ 5s ²	53 I 126.90 [Kr] 4d ¹⁰ 5s ²	54 Xe 131.30 [Kr] 4d ¹⁰ 5s ²
55 Cs 132.91 [Xe] 6s ¹	56 Ba 137.34 [Xe] 6s ²	57 La 138.91 [Xe] 5d ¹ 6s ²	58 Ce 140.12 [Xe] 5d ¹ 6s ²	59 Pr 140.91 [Xe] 5d ¹ 6s ²	60 Nd 144.24 [Xe] 5d ¹ 6s ²	61 Pm 144.91 [Xe] 5d ¹ 6s ²	62 Sm 150.35 [Xe] 5d ¹ 6s ²	63 Eu 151.96 [Xe] 5d ¹ 6s ²	64 Gd 157.25 [Xe] 5d ¹ 6s ²	65 Tb 158.92 [Xe] 5d ¹ 6s ²	66 Dy 162.50 [Xe] 5d ¹ 6s ²	67 Ho 164.93 [Xe] 5d ¹ 6s ²	68 Er 167.26 [Xe] 5d ¹ 6s ²	69 Tm 168.93 [Xe] 5d ¹ 6s ²	70 Yb 173.04 [Xe] 5d ¹ 6s ²	71 Lu 174.97 [Xe] 5d ¹ 6s ²	72 Hf 178.49 [Xe] 5d ² 6s ²
87 Fr (223) [Rn] 7s ¹	88 Ra 226.025 [Rn] 7s ²	89 Ac 227.0 [Rn] 6d ¹ 7s ²	90 Th 232.04 [Rn] 6d ² 7s ²	91 Pa 231 [Rn] 6d ¹ 7s ²	92 U 238.03 [Rn] 6d ¹ 7s ²	93 Np 237 [Rn] 6d ¹ 7s ²	94 Pu 242 [Rn] 6d ¹ 7s ²	95 Am 243 [Rn] 6d ¹ 7s ²	96 Cm 247 [Rn] 6d ¹ 7s ²	97 Bk 247 [Rn] 6d ¹ 7s ²	98 Cf 249 [Rn] 6d ¹ 7s ²	99 Es 254 [Rn] 6d ¹ 7s ²	100 Fm 253 [Rn] 6d ¹ 7s ²	101 Md 258 [Rn] 6d ¹ 7s ²	102 No 253 [Rn] 6d ¹ 7s ²	103 Lw [Rn] 6d ¹ 7s ²	104 Eka-Lw [Rn] 6d ¹ 7s ²